# Ca-Mm-Ni BASED HYDROGEN STORAGE ALLOYS

## Field of the invention

The present invention relates to new Ca-Mm-Ni based alloys of the $AB_5$ type.

The invention also relates to a process for preparing these new alloys and to the use of such new alloys for hydrogen storage.

## Background of the invention

The use of hydrogen gas as a fuel for PEM fuel cells has received considerable attention in recent years in view of the fact that PEM fuel cells using pure hydrogen can provide high efficiency and ultra clean power. Unfortunately, the widespread use of hydrogen energy is limited by economic and technological barriers. One of the important barriers is the lack of cost effective, safe hydrogen storage method.

Hydrogen gas is very light. It can be compressed under high pressure and stored in pressurized vessels. It can also be liquefied and stored in liquid form. Hydrogen also reacts with metal or non-metals to form hydrides. Some metal hydrides are reversible at ambient temperature and pressures. From a safety point of view, metal hydrides are intrinsically safe since the hydrogen must be released from the hydrides by an endothermic process before it can burn or be oxidized.

The volumetric density of hydrogen storage in metal hydrides is usually high. The most serious shortcomings of the reversible low temperature metal hydrides are their low gravimetric storage density and their high cost. For stationary and some mobile applications, the weight of the hydrogen storage tank is not a problem. However, the high cost of conventional low temperature metal hydrides results in too expensive storage devices.

$CaNi_5$ intermetallic compound represents a category of low cost hydrogen storage materials with a maximum storage capacity up to 1.9wt.% (see reference 1). However, little attention has been paid to this system, probably due to its well-known bad cycling stability (see reference 2). Improvement of

the hydrogen storage properties of $CaNi_5$ by substitution of Ca or Ni with other elements has been tried (see references 3 to 5). Ternary $Ca_xMm_{1-x}Ni_5$ and quaternary $Ca_xMm_{1-x}Ni_{5-y}Cu_y$ alloys have been produced by melt casting and patented 20 years ago (see reference 6). Substitution of Mm (mishmetal) for Ca can raise the plateau pressure of $CaNi_5$. However, the plateau slope is big for the as-cast ternary alloys due to segregation. Annealing at elevated temperatures (>1000C) can reduce the slope to some extent. The inventor's previous work show that $CaNi_5$ and Mm and/or Zn-substituted $CaNi_5$ type alloys with flat plateau can be successfully produced (see reference 7).

Substitution of Ni by Mm and Al in the $CaNi_5$ type alloys can improve the cycling stability as disclosed in US 4,631,170 (see reference 8). However, the long term cycling stability of the alloys according to this patent is still not good enough. Typically more than 20% of the capacity is lost upon 200 times of hydrogen absorption/desorption cycling.

Further improvement has been achieved by concomitant substitution of Mm for Ca and Zn and Al for Ni, as reported by the present inventors of record (see reference 9). The capacity loss after 500 cycles has proved to be less than 20% for $Ca_{0.8}Mm_{0.2}Ni_{4.8}Zn_{0.1}Al_{0.1}$ and less than 10% for $Ca_{07}Mm_{0.3}Ni_{4.8}Al_{0.1}Zn_{0.1}$. However, the maximum storage capacity is significantly reduced by substitution of Zn and Al for Ni.

## Summary of the invention

In accordance with the present invention, it has now been found that substitution of Si, Ge and some other metalloid elements (also called "semi-metals") for Ni in a ternary Ca-Mm-Ni alloy of the $AB_5$ type can substantially improve the long term stability of such an alloy without causing much reduction of the storage capacity. Essentially, no capacity loss has been observed after 500 hydrogen absorption and desorption cycles.

Thus, a first object of the present invention is to provide new Ca-Mm-Ni based alloys of the $AB_5$ type, which are capable of absorbing and desorbing hydrogen from a gas phase at ambient temperature with a relative flat plateau

pressure and a storage capacity larger than 1.2wt.%. These new alloys are of the formula (I):

$$(Ca_xM_{1-x})_t(Ni_{1-y}T_y)_5 \qquad (I)$$

where M is selected from the group consisting of: any mischmetal, any rare earth metal, and an homogeneous or an inhomogeneous combination of any of: (i) at least two mischmetals, (ii) at least two rare earth metals, and (iii) at least one mischmetal and at least one rare earth metal.

T is selected from the group consisting of metalloids and an homogeneous or an inhomogeneous combination of at least two metalloids;

$0<x\leq 1$;

$0<y\leq 0.5$ and

$0.8 \leq t \leq 1.2$.

Another object of the invention is to provide a process for the preparation of the above mentioned alloys of formula (I), which comprises the following steps:

a) preparing a powder by milling a mixture of elemental powders and/or pre-alloyed substances of the elemental ingredients of the alloy to be prepared (such as, for example, Ca, Ni, Mm, $CaNi_2$, $CaNi_5$, $MmNi_5$ and so on) in adequate proportions to obtain the required alloy; and

b) annealing and/or sintering the so prepared powder at elevated temperatures in a crucible for a short period of time in an inert or reactive atmosphere.

In use, step a) may consist of a ball milling or of a mechanical alloying and can be carried out at room temperature or at high temperatures with or without anti-sticking agents.

Step b) is essential to the above process. This step must actually be carried out to achieve high reversible capacity and a flat plateau. In use, the annealing can be carried in a crucible made of stainless steel at a temperature higher than 600°C but not higher than 1100°C.

Alternatively, the new compounds according to the invention can be produced by conventional melt casting methods or powder sintering methods.

The compounds according to the invention are useful for hydrogen storage in a gaseous form and such is a further object of the invention.

**DETAILED DESCRIPTION OF THE INVENTION**

As aforesaid, the invention is directed to new alloys of the $AB_5$ type, which are of the formula:

$(Ca_xM_{1-x})_t(Ni_{1-y}T_y)_5$

M can be mischmetal, or any rare earth metal. M can also be an homogeneous or an inhomogeneous combination of any of: (i) at least two mischmetals, (ii) at least two rare earth metals, and (iii) at least one mischmetal and at least one rare earth metal. In this respect, M is selected from the group consisting of any mischmetal, any rare earth metal, and an homogeneous or an inhomogeneous combination of any of: (i) at least two mischmetals, (ii) at least two rare earth metals, and (iii) at least one mischmetal and at least one rare earth metal

T is selected from the group consisting of: metalloids, and an homogeneous or an inhomogeneous combination of at least two metalloids;

$0<x\leq 1$ (x‡0), preferably $0.4<x\leq 1$;

$0< y \leq 0.5$ (y‡0), preferably $0<y\leq 0.3$; and

$0.8 \leq t \leq 1.2$.

A suitable mischmetal is one of the composition 51 wt% Ce, 26.4 wt% La, 16.4 wt% Nd and 5.3 wt%Pr. A further suitable mischmetal is one of the

composition 62 wt% La, 21 wt%Ce, 3 wt% Pr, and 14 wt% Nd. Many further compositions are suitable, and differ in the properties of the constituent elements La, Ce, Pr, and Nd.

Examples of rare earth metals are Y, La, Ce, Pr, Nd, Sm, Dy, Gd, Ho, Th, U, Pm, Tb, Er, and Lu. Preferably, the rare earth metal is any of La, Ce, Pr, Nd, Dy, Th, and Y.

Suitable metalloids include Si, Ge, and Ga.

As aforesaid, the invention is actually based on the discovery that significant further improvements have been achieved by substituting Si, Ge and/or other metalloids for Ni in the above mentioned Ca-Mm-Ni alloy of the $AB_5$ type (see the definition of T in the formula given hereinabove). This substitution has significant effect of improving the long-term stability while keeping predominantly the $AB_5$ structure and hydrogen storage capacity according to the invention that are particularly useful.

The new Ca-Mm-Ni alloys of the $AB_5$ type according to the invention with improved properties can be made by mechanical alloying of elemental powders (such as Ca, Mm, $Ni_5$) and/or mixtures of intermetallic compounds (such as $CaNi_5$, $MmNi_5$) corresponding to the required composition, followed by an thermal annealing treatment at temperatures higher than 600°C for short period of time, typically at 1000°C or slightly higher for 0.5h-lh in a steel crucible. Annealing at temperatures lower than 600C does not improve the hydrogen storage properties very much.

The invention and its advantages will be better understood upon reading the following description made with reference to the accompanying drawings.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Fig. 1 is a curve giving the hydrogen storage capacity of an alloy of formula $(Ca_{0.64}\ Mm_{0.36})_{1.1}\ Ni_5$ as a function of the pressure after 3 cycles and 250 cycles;

Fig. 2 is a curve similar to the one of Fig. 1, but with an alloy of formula $(Ca_{0.64}\ Mm_{0.36})_{1.1}\ Ni_{4.9}\ Si_{0.1}$;

Fig. 3 is a curve similar to the one of Fig. 1, but with an alloy of formula $(Ca_{0.64}\ Mm_{0.36})_{1.1}\ Ni_{4.8}\ Si_{0.2}$;

Fig. 4a is a X-ray analysis of the alloy of formula $(Ca_{0.64}\ Mm_{0.36})_{1.1}\ Ni_{4.8}\ Si_{0.2}$ mentioned hereinabove (see Fig. 3);

Fig. 4b is an X-ray analysis of the alloy of formula $(Ca_{0.64}\ Mm_{0.36})_{1.1}\ Ni_5$ mentioned hereinabove (see Fig. 1); and

Fig. 5 is a curve similar to the one of Fig. 1, but with an alloy of formula $(Ca_{0.64}\ Mm_{0.36})_{1.1}\ Ni_{4.85}\ Ge_{0.15}$.

**EXAMPLE 1** (Preparation of a known compound by the process of the invention)

$(Ca_{0.64}Mm_{0.36})_{1.1}Ni_5$ was synthesized by mechanical alloys in a SPEX high energy ball mill under argon. A $MmNi_5$ powder (>99%, + 100mesh), Ca granules (>99.5, ~2mm in size) and Ni powders (<99.9%,-325mesh) were used as starting materials.

After alloying, an isothermal annealing was performed in a tubular furnace under argon. The mechanically alloyed powder was sealed in a stainless steel crucible before annealing. The powder was heated to 1050°C at a heating rate of 30°C/min, and held at 1050°C for 1 hour, then cooled down to room temperature in the furnace.

The hydrogen absorption/desorption properties were measured by using an automatic Sievert's type apparatus. The annealed powder normally needs mild activation treatment, such as heated to 200°C under vacuum and then cooled down. The activated $(Ca_{0.64}Mm_{0.36})_{1.1}\ Ni_5$ alloy exhibits a relative flat plateau and a maximum storage capacity of 1.44 wt.% under 4.0MPa of charging pressure.

A hydrogen absorption/desorption cycling experiment was performed at 30°C under an absorption pressure of 3.5MPa and a desorption pressure of 0.01MPa. The absorption and desorption time was 12 minutes respectively. Under these conditions, the alloys could be fully hydrided and dehydrided. The hydrogen purity was 99.999%. As shown in Fig. l, the maximum storage capacity was reduced to 1.23 wt. % after 250 cycles (20% loss). The reduction of the effective reversible storage capacity is even bigger.

**EXAMPLE 2** (Compound according to the invention made by the process of the invention)

$(Ca_{0.64}Mm_{0.36})_{1.1}Ni_{4..9}Si_{0.1}$ was synthesized by mechanical alloying of elemental Ca, Si and $MmNi_5$ powder blends. The alloy was annealed in the same manner as in Example 1. This alloy had a maximum hydrogen storage capacity of 1.4wt.%. The maximum hydrogen storage capacity are slightly reduced by 8% after 250 cycles as shown in Fig.2 in contrast to the 20% loss in the $(Ca_{0.64}Mm_{0.36})_{1.1}Ni_5$.

**EXAMPLE 3** (Compound according to the invention made by the process of the 30 invention)

$(Ca_{0.64}Mm_{0.36})_{1.1}Ni_{4.8}iSi_{0.2}$ was synthesized by mechanical alloying of elemental Ca, Si and $MmNi_5$ powder blends. The alloy was annealed in the same manner as in Example 1. This alloy had a hydrogen storage capacity of 1.3wt.%. The maximum and reversible hydrogen storage capacities are slightly improved upon hydrogen absorption and desorption cycling as shown in Fig.3.

X-ray analyses show that Si-substituted alloys have very high resistance to peak broadening upon cycling as shown in Fig.4a. While the $(Ca_{0.64}Mm_{0.36})_{1.1}Ni_5$ alloy without Si substitution shows obvious peak broadening after cycling as shown in Fig. 4b. It was believed that hydrogen absorption/desorption cycling introduces defects, such as microstrain, chemical disorders and grain boundaries (reduced grain size), therefore leads to reduced storage capacity. The peak broadening reflects the defects introduced during cycling experiments.

**EXAMPLE 4** (Compound according to the invention made by the process of the invention)

$Ca_{0.7}$ $Mm_{0.4}Ni_{4.85}Ge_{0.15}$ was synthesized by mechanical alloying of elemental powder blends. The alloy was annealed in the same manner as in Example 1. This alloy had a maximum hydrogen storage capacity of 1.3wt.% in the as-synthesized state. Substantial improvement in the maximum and reversibly storage capacity is observed after 500 cycles as shown in Fig.5.

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